<Preliminary>A Role of Oxalic Acid in Acid Hydrolysis of Non-Phenolic β-O-4 Type Lignin Carbohydrate Complexes (LCC) Model Compounds

AUTHOR(S):

TOKIMATSU, Toshiaki; UMEZAWA, Toshiaki; SHIMADA, Mikio

Preliminary

A Role of Oxalic Acid in Acid Hydrolysis of Non-Phenolic β-*O*-4 Type Lignin Carbohydrate Complexes (LCC) Model Compounds*[1]

Toshiaki TOKIMATSU*[2], Toshiaki UMEZAWA*[2]
and Mikio SHIMADA*[2]

(Received May 31, 1995)

Keywords : oxalic acid, lignin model, lignin carbohydrate complex, brown-rot fungi, acid hydrolysis.

Brown-rot fungi accumulate a considerable amount of oxalic acid in their culture media[1-3]. Actually, significant amounts of oxalic acid was determined from the wood meal decayed by a brown-rot fungus[4]. Green *et al.* have recently reported that the pH at the site of the decaying wood block which had been inoculated with a brown-rot fungus *Poria placenta* dropped to 1.7 within a week[5]. It has also been reported that the treatments of cellulose and wood meals with the oxalic acid solution caused decrease in the cellulose viscosity and the liberation of free sugars from the wood meals[6]. In consideration of the acid catalysis by oxalic acid and its production by brown-rot fungi, the acid hydrolysis of wood components may also be important in brown-rot wood decay processes although the effect of Fenton type oxidation[7,8] seems to have been emphasized.

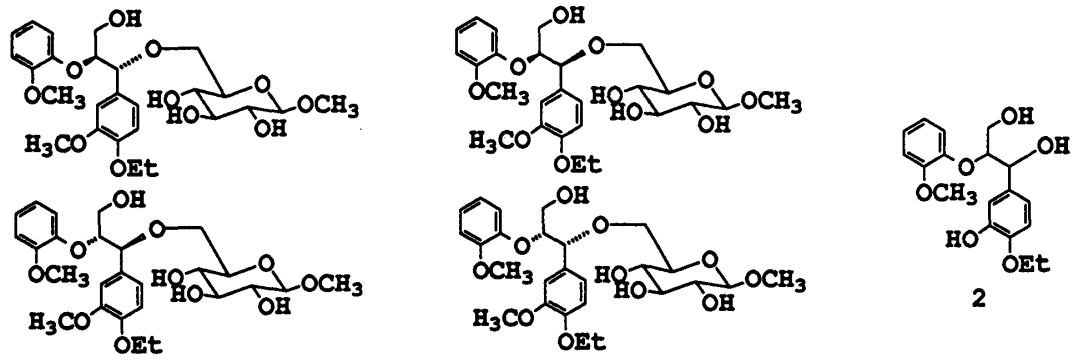
In this context, it is important to investigate stability of lignin carbohydrate complexes (LCC) in the oxalic acid solution in relation to the brown-rot decay. Therefore, we examined first the acid hydrolysis of β-*O*-4 type LCC model compounds (**1**), whose stereoisomers (Fig. 1) were synthesized in stereochemically pure forms[9].

Each diastereomer of (**1**) was incubated at 37°C for 12 days with 0.1 M oxalic acid solution (pH 1.8) (final concentration of LCC model compound 0.38 mM). The product was identified as the aglycone of the LCC substrate (**2**) by GC-MS (Fig. 1). The amount was determined with an internal standard of 4-*O*-ethyldihydroconiferyl alcohol on HPLC; the aliquots were taken out from the reaction mixtures at 3-day intervals for quantitative analysis.

Fig. 2 shows the time course of the formation of the product during the incubation periods, indicating the yield of the product formed from each isomer after 12-day incubation

*[1] A part of this work was presented at the 44th Annual Meeting of the Japan Wood Research Society in Nara, April 1994.

*[2] Laboratory of Biochemical Control.



***Erythro*-form ($1e_1$, $1e_2$)** ***Threo*-form ($1t_1$, $1t_2$)**

2

Fig. 1. Diastereomeric Lignin Carbohydrate Complexes (LCC) Model Compounds (**$1e_1$**, **$1e_2$**, **$1t_1$** and **$1t_2$**) and Hydrolyzed Product (**2**).
Et: —OCH_2CH_3.

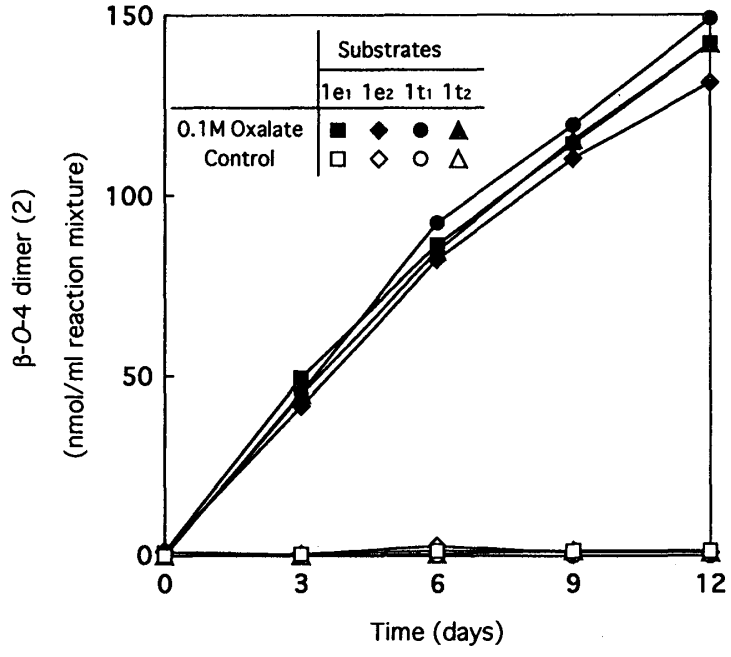


Fig. 2. Formation of *β-O*-4 dimer (**2**).

is about 30%. Since there was no significant difference in the reaction rates either among the all isomers or between the *erythro* and *threo* forms, the C_α-ether linkage of the all stereoisomers are equally unstable under the present incubation condition.

In conclusion, during the long duration of brown-rot wood decay, oxalic acid produced may play a multiple key role in breaking down the LCC linkage as well as glycosidic linkages in hemicellulose and amorphous regions of cellulose in wood, because the acid present in a relatively smaller amount to Fe(III) in the reaction site accelerated the degradation of cellulose by Fenton oxidation, but inhibited the Fenton oxidation at larger concentrations[10].

References

1) H. SHIMAZONO and K. TAKUBO: *Bull. Forest. Exp. Station,* **53**, 117–125 (1952).
2) S. TAKAO: *Appl. Microbiol.,* **13**, 732–737 (1965).
3) Y. AKAMATSU, M. TAKAHASHI and M. SHIMADA: *Material und Organismen,* **28**, 251–264 (1994).
4) H. SHIMAZONO: *J. Jpn. Fores. Soc.,* **33**, 393–397 (1951).
5) F. GREEN III, M.J. LARSEN, J.E. WINANDY and T.L. HIGHLY: *Material und Organismen,* **26**, 191–213 (1991).
6) M. SHIMADA, Y. AKAMATSU, A. OHTA and T. TAKAHASHI: Intern. Res. Group./Wood Preserv. Document, No. IRG/WP 1472 (1991).
7) J.W. KONIGS: *Wood and Fiber,* **6**, 66–80 (1974).
8) C.J. SHIMIDT, B.K. WHITTEN and D.D. NICHOLAS: *Am. Wood Preserv. Assoc.,* **77**, 157–164 (1981).
9) T. TOKIMATSU, T. UMEZAWA and M. SHIMADA: *Holzforsch.* (1995, in press).
10) N. TANAKA, Y. AKAMATSU, T. HATTORI and M. SHIMADA: *Wood Research,* No. **81**, 8–10 (1994).